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Raman Scattering of Light by Molecules of Methyl Orange Dye on the Surface of Silicon Containing Ion-Synthesized Silver Nanoparticles

V. V. Vorob'ev[a, *], A. M. Rogov[a], Yu. N. Osin[a], N. N. Brandt[b], V. I. Nuzhdin[c], V. F. Valeev[c], and A. L. Stepanov[a, c]

[a] *Interdisciplinary Center for Analytical Microscopy, Kazan (Volga Region) Federal University, Kazan, 420021 Russia*

[b] *Faculty of Physics, Moscow State University, Moscow, 119991 Russia*

[c] *Group of Nano-Optics and Nano-Plasmonics, Zavoisky Kazan Physical Technical Institute, Kazan Scientific Center, Russian Academy of Sciences, Kazan, 420029 Russia*

**e-mail: slava.v679@gmail.com*

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Abstract—The possibility of using a new composite material based on porous silicon containing silver nanoparticles and synthesized by means of a unique implantation nanotechnology as an optically sensitive material in biological and chemical sensors is tested experimentally. It is demonstrated that detection of small amounts of the studied organic substance (methyl orange dye) is possible due to the effect of surface-enhanced Raman scattering (SERS) from the molecules affected by the local electromagnetic field of the silver nanoparticles.

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INTRODUCTION

Raman-scattering spectroscopy is currently one of the most efficient analytical methods of detection and investigation of organic substances, because the difference in the frequencies of the incident and scattered optical radiation is equal to the frequency of the intramolecular vibrations, which is a particular characteristic of the studied molecule. However, the efficiency of Raman scattering is relatively small relative to that of, e.g., fluorescence. Therefore, a search for various solutions for increasing Raman signal intensity continues. Raman-scattering spectroscopy received a boost in 1974 when M. Fleischmann proposed using a silver electrode subjected to anode etching to increase the surface area for adsorption of pyridine molecules [1]. It was discovered that the Raman signal increased by six to seven orders of magnitude relative to that obtained from a smooth electrode, whereas the effective area of the electrode increased by only one order of magnitude, suggesting that the surface-area contribution was not dominant. The effect of an increase in intensity of Raman scattering on a rough metal surface was named the "effect of surface-enhanced Raman scattering" (SERS). In addition to on rough metal substrates, the effect of SERS was observed in a system of organic substances containing nanoparticles of noble metals (silver, gold, copper, platinum). Incident electromagnetic waves drive resonance oscillations of conduction electrons in such nanoparticles, which are referred to as "surface plasmon resonance" [2]. A locally enhanced electromagnetic field appears in the vicinity of a metal nanoparticle, and, when an analyzed molecule is located within this close-range field, the intensity of its Raman scattering increases; i.e., the SERS effect takes place [3]. This mechanism of enhancement of Raman scattering is called "electromagnetic." The optical signal from the molecules should not be mixed with the Raman scattering from the metal nanoparticles themselves, which is induced by their acoustic oscillations [4]. The efficiency of SERS depends on the structure of substrates containing metal nanoparticles, as well their granulometric parameters, the type of metal, etc. In addition to the electromagnetic description, the effect of enhancement of Raman scattering is explained in the literature as being due to a chemical mechanism that takes place upon adsorption of molecules on metal nanoparticles. Such an interaction can lead to charge transfer between a molecule and a metal nanoparticle. Numerical estimates show that the electromagnetic mechanism can cause enhancement of the Raman signal by up to seven orders of magnitude, while chemical adsorption can lead to an enhancement by two to three orders of magnitude, although distinguishing the contributions of each mechanism is difficult in practice [5].